



Catalytic combustion of polycyclic aromatic hydrocarbons (PAHs) over zeolite type catalysts: Effect of water and PAHs concentration

S.C. Marie-Rose^a, T. Belin^a, J. Mijoin^{a,*}, E. Fiani^b, M. Taralunga^c, F. Nicol^c, X. Chaucherie^c, P. Magnoux^a

^a Université de Poitiers, Laboratoire de Catalyse en Chimie Organique, UMR CNRS 6503, 40 av. du Recteur Pineau, 86022 Poitiers Cedex, France

^b Agence De l'Environnement et de la Maîtrise de l'Energie (ADEME), 20 av. Du Grésillé – BP 90406, 49004 Angers Cedex 01, France

^c Centre de Recherche sur la Propreté et l'Energie (CRPE), 291 av. Dreyfous Ducas, 78520 Limay, France

ARTICLE INFO

Article history:

Received 22 January 2009

Received in revised form 26 March 2009

Accepted 28 March 2009

Available online 16 April 2009

Keywords:

Methylnaphthalene

Water cluster

Faujasite

USHY

Platinum

ABSTRACT

The catalytic combustion of 1-methylnaphthalene (1-MN), a PAH representative molecule, was carried out over USHY and 0.8%PtUSHY catalysts in presence of steam. These catalysts are able to transform low concentration of 1-MN into carbon dioxide at 300 °C over USHY catalyst and at 200 °C over PtUSHY, without by-products formation. The presence of platinum on the USHY increases the catalytic activity, hence the reaction rate. The influence of platinum content showed that 0.5% of platinum deposited on the zeolite was sufficient to oxidize 900 ppm of 1-MN at 300 °C.

The influence of water content in the feed was investigated and several assumptions were put forth to explain our results. The carbon dioxide yield decreases in the 0–12% range of relative humidity (RH). When RH increases up to 12% the carbon dioxide yield increases. Over USHY catalyst and for low water content (RH < 12%), water could be adsorbed over strong hydrophylic sites of USHY zeolite or via H₂O dimer (neutral complex form) formation. Over PtUSHY catalysts, water adsorption over the PtO phase could be considered. For high water content (RH > 12%), water cluster formation via H₂O dimer (ion-pair complex form) is proposed on both catalysts. This form of H₂O dimer (ion-pair complex) could generate an acidity, which facilitates the formation of oxygenated compounds easily degradable into carbon dioxide.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Reducing the emissions of toxic substances such as POPs (persistent organic pollutants) is one of the major problems faced by industrialized countries. POPs include a wide range of pollutants, which are semi-volatile, bioaccumulative, persistent and toxic. The POP's family includes polychlorodibenzodioxins (PCDDs also called dioxins), polychlorodibenzofurans (PCDFs also called furans), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). Their presence in the environment is harmful to humans but also to the ecosystems. Hence, these pollutants have received special attention for the last 10 years [1]. POPs are by-products of incomplete combustion and are formed in many types of combustion and thermal processes. As the APC (Air Pollution Control) technology has been greatly improved over the last years, new R&D routes are investigated to control POPs trace emissions. Catalytic destruction of these pollutants to CO₂, H₂O

and HCl (in the case of chlorinated compounds) appears very promising in this context.

The metal oxides or noble metals supported catalysts have already been studied to destroy organic pollutants. Metal oxide supported on Al₂O₃ demonstrated to be the most active catalyst for the destruction of PAHs model compounds and mainly naphthalene [2]. In the literature, there is a limited number of studies about PAHs catalytic combustion. These studies are almost exclusively focused on naphthalene total combustion on different noble metal and some supported metal oxide catalysts, such as Pt, Pd, Ru, Co, Mo and W supported on γ -Al₂O₃ [2–4]. However, platinum is one of the most used noble metal in the literature for hydrocarbons oxidation [2,5–12]. In addition, naphthalene catalytic oxidation in a gas mixture simulating emissions from combustion of biofuels was studied [12–14]. Catalytic oxidation of PAHs mixtures in Waste-to-Energy exhaust gas was also investigated: V₂O₅/TiO₂ and V₂O₅-WO₃/TiO₂ catalysts showed to be highly efficient for removing gas phase PAHs at very low temperature [15,16]. However, if most of the studies deal with the observed conversion of the PAHs, only few are taking into account the selectivities of these catalysts. Indeed, V₂O₅/TiO₂ and V₂O₅-WO₃/TiO₂ could lead the formation of by-products, and the selectivity towards CO₂ is

* Corresponding author. Tel.: +33 5 49 45 39 12; fax: +33 5 49 45 37 79.

E-mail address: jerome.mijoin@univ-poitiers.fr (J. Mijoin).

not really satisfactory since CO is often produced in non-negligible amounts [17]. Therefore, the development of more selective and cost-effective catalysts for complete oxidation of PAHs needs to be carried out. In this context, acid zeolites have recently gained interest as alternative catalysts to metal oxides for hydrocarbon oxidation [10,18–23]. Faujasite zeolite type was used as catalyst for 1,2-dichlorobenzene [21], mixtures of 1,2-dichlorobenzene/benzofuran [20] and 1-methylnaphthalene/1,2-dichlorobenzene [24] combustion. The performance of this zeolite type can be associated with the strength of Brønsted acid sites.

Generally, steam is present in polluted exhaust and the effect of water vapour content was studied in the case of PCDD/F decomposition [25]. Water vapour plays two important roles in the catalytic reaction [26,27]. Firstly, via the competitive adsorption mechanism, water vapour may reduce the contact between PCDD/F molecules and the active sites of the catalysts and hence inhibits the reaction rate. On the other hand, steam can also facilitate the removal of chlorine present on the catalyst surface during oxidation of chlorinated pollutants [26].

In the literature, few studies deal with catalytic destruction of PAHs over zeolite catalysts. The aim of this work is to show in presence of steam the potential of zeolite as catalyst for oxidation of PAHs without by-products formation. In this work, 1-methylnaphthalene (1-MN) was used as a model molecule representative of PAHs: it possesses two condensed aromatic rings, which are the characteristic of all PAHs, and is liquid and relatively volatile at ambient temperature. The catalytic oxidation of 1-MN was studied over faujasite type zeolite catalyst. Zeolite doped with platinum were also studied since previous works on chlorinated aromatics showed their high activities and selectivities with low formation of polychlorinated by-products generally observed over supported platinum [20,28]. We also examined several parameters, which can affect this reaction: the influence of Si/Al zeolites framework ratio, the platinum content on USHY zeolites, the reaction time (stability) and the effect of water and of 1-MN concentrations in the feed.

2. Experimental

2.1. Catalysts preparation

Faujasite zeolites were supplied by Zeolyst Corporation. PtUSHY catalysts were prepared by ion exchange with $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ salt at pH between 6 and 7, with continuous stirring for 24 h at room temperature. The exchanged samples were filtered, washed and dried at 100 °C overnight. Then, catalysts were calcined under dry airflow (150 mL min^{-1}) at 350 °C during 6 h (temperature program: 1 °C min^{-1} from ambient temperature to 100 °C, 1 h at 100 °C, then 1 °C min^{-1} to 350 °C). The Pt catalysts were labelled as follows: xPtUSHY with x for the percentage of Pt.

2.2. Catalysts characterization

Acidity of the catalysts was characterized by pyridine adsorption followed by IR spectroscopy. IR spectra were recorded with a Nicolet Magna IR spectrometer using thin wafers of 5–15 mg cm^{-2} activated *in situ* in the IR cell under secondary vacuum (10^{-3} Pa) at 200 °C for 2 h. Pyridine was adsorbed on the sample at 150 °C. The IR spectra were recorded at room temperature after activation and pyridine thermodesorption under vacuum (10^{-3} Pa) for 1 h at 150 °C. Concentrations of Brønsted and Lewis sites able to retain pyridine adsorbed at 150 °C were determined from the normalised absorbance areas of the bands at 1545 and 1450 cm^{-1} , respectively using extinction coefficients previously determined [29].

Platinum contents were determined externally by the “Service Central d’Analyse” of the CNRS, Vernaison, France. Platinum

dispersion was determined by CO adsorption followed by IR spectroscopy [30]. The IR spectra were recorded with a Nicolet Magna IR 750 spectrometer. Before adsorption, the catalyst was reduced under hydrogen flow (80 mL min^{-1}) at 400 °C overnight.

Catalytic samples were also characterized before reaction by nitrogen adsorption at –196 °C using an ASAP 2000 (Micrometrics) gas adsorption system to determine the microporous volume thanks to the Dubinin–Radushkevich equation [31].

The carbon content deposited after reaction on catalysts was measured by total burning at 1020 °C under helium and oxygen with a Thermoquest NA2910 analyser.

The adsorbed molecules (“coke”) retained on the catalyst after reaction were characterized by IR spectroscopy. The IR spectrum was recorded with a Nicolet Magna IR spectrometer using thin wafers of 5–15 mg cm^{-2} activated *in situ* in the IR cell at 150 °C during 2 h. The IR spectra were recorded at room temperature.

2.3. 1-Methylnaphthalene transformation

Before oxidation reaction, the samples were pelletized, crushed and sieved to obtain a grain size between 0.2 and 0.4 mm, then calcined under dry air at 500 °C for 4 h. The oxidation of 1-methylnaphthalene (1-MN) was carried out at a constant temperature in a fixed bed reactor containing 115 mg of catalyst. For each experiment, a new catalyst sample was used and the reactions were monitored as a function of time. 1-MN and water were introduced by mean of two saturators (one kept at ambient temperature for water and the other heated for the 1-MN to obtain the desired concentration). The composition of the feed in standard condition was close to 600 ppm (3.64 g m^{-3}) of 1-MN and 1.03% of water (corresponding to a relative humidity of about 50% at 25 °C) in air. USHY zeolite are known to be stable in humid conditions, because of the dealumination process they underwent. It was shown that moderately dealuminated Y zeolites (like the one used in this study) are stable up to 400 °C even in almost pure water vapour [32]. For technical reasons, experiments could not be carried out at higher water content, but thanks to their resistance in humid flows and assuming that adsorption competition should not really occur between 1-MN and water according to the differences of polarity and hydrophilic character, it seems reasonable to consider that 1MN conversion should persist at higher water partial pressures. The total gas flow was 65.4 mL min^{-1} corresponding to a VVH of $20,000 \text{ h}^{-1}$. The reaction products were analyzed on-line by a gas chromatograph (Varian 3400) equipped with a FID and a TCD detector and respectively a CP-SIL 8 column for the analysis of the organic products and a Porapak Q column for CO_2 analysis. The eventual production of CO was measured by means of specific Dräger® tubes.

3. Results and discussion

Whatever the reaction temperature and the operating conditions, in our conditions only carbon dioxide was observed as oxidation products. No hydrocarbon by-products were observed.

3.1. Oxidation of 1-methylnaphthalene (1-MN) over faujasite zeolites

3.1.1. Effect of Si/Al ratio on 1-MN oxidation

Oxidation of 1-MN (627 ppm) was carried out over various faujasite type zeolites (HFAU) with a framework Si/Al ratio varying from 5 to 100. The characteristics of these zeolites are given in Table 1. The CO_2 yield taken after 6 h reaction as a function of reaction temperature is shown in Fig. 1. As in the case of coke oxidation [33], it appears that the most acidic zeolites (USHY and HFAU (17)) are the best ones for the 1-MN oxidation. Thus, these zeolites are able to completely oxidize 1-MN into carbon dioxide

Table 1
Physicochemical properties of HFAU catalysts.

Zeolites	(Si/Al)	Acidity ($\mu\text{mol g}^{-1}$) ^a		V_{micro}^b ($\text{cm}^3 \text{g}^{-1}$)
		Brønsted	Lewis	
USHY	5	537	168	0.290
HFAU	17	272	101	0.257
HFAU	47	99	15	0.245
HFAU	100	53	12	0.313

^a Brønsted and Lewis acids sites concentrations determined by pyridine adsorption followed by IR spectroscopy.

^b V_{micro} (microporous volume) measured by BET.

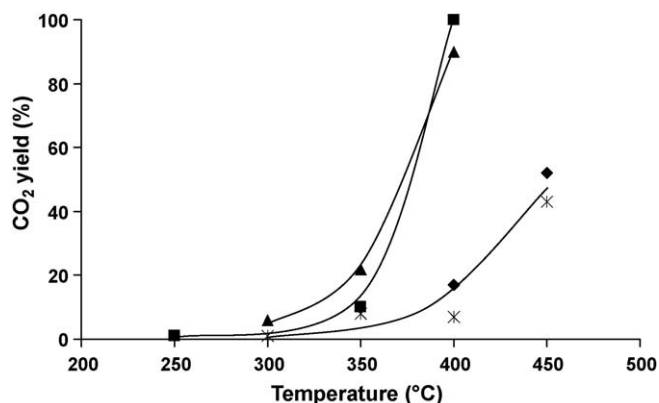


Fig. 1. Carbon dioxide yield after 6 h reaction as a function of the reaction temperature over faujasite type zeolites: USHY (▲), HFAU (17) (■), HFAU (47) (◆) and HFAU (100) (*). Initial 1-MN concentration = 627 ppm, VVH = 20,000 h⁻¹, RH = 50%.

above 400 °C while only 10 and 20% of 1-MN can be oxidized into carbon dioxide over HFAU (100) and HFAU (47), respectively. Indeed, oxidation reaction needs a catalyst, which possesses a sufficient number of Brønsted acids sites for the reaction what is not the case for HFAU (47) and HFAU (100) (Table 1). As mentioned by Moljord et al. [34], the density of framework aluminium atoms, hence of zeolite acid sites, is the determining parameter for the reaction. As USHY appears to be as an appropriate support, this zeolite was chosen for the following study.

3.1.2. Oxidation of 1-MN over USHY zeolite

Oxidation of 1-MN (900 ppm) was carried out over USHY zeolite at various temperatures (from 300 to 450 °C). Fig. 2 reports the 1-MN conversion and carbon dioxide yield as a function of the reaction time. 1-MN was completely transformed at 450 °C and the CO₂ yield increased continuously up to 100%. At 400 and 300 °C, the initial conversion of 1-MN was total, but after a few minutes a deactivation occurred (Fig. 2a). However, if the reactant initially disappeared, the yield into carbon dioxide was not equal to 100% (Fig. 2b). The difference between the disappearance of 1-MN and the carbon dioxide yield is due to the adsorption of the reactant and/or coke formation. The carbon contents measured after 6 h reaction over the samples were 11.0, 9.9 and 4.1 wt% for 300, 400 and 450 °C, respectively. The carbon balance was close to 100%, if we consider that the difference between 1-MN transformation and carbon dioxide yield is due to coke formation (or 1-MN adsorption). Indeed, the theoretical percentages of carbon deposited over zeolite after 6 h reaction were calculated and found equal to 9.6, 7.0 and 3.0 wt% for 300, 400 and 450 °C, respectively. Carbon monoxide (CO) was never detected. This observation is inconsistent with results of Moljord et al. who found a CO/CO₂ ratio of about 0.47 at 400 °C during coke combustion [35]. The absence of CO could

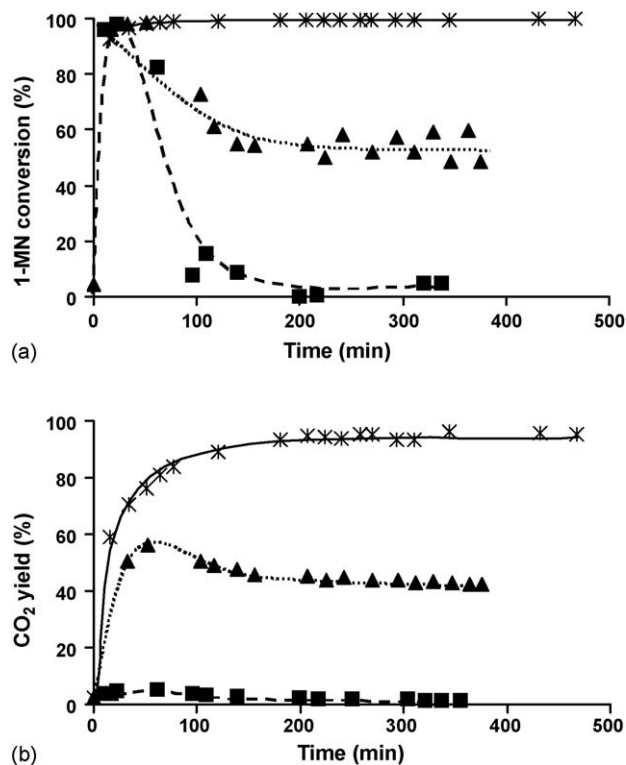


Fig. 2. Influence of time on the global conversion of 1-methylnaphthalene (a) and on the carbon dioxide yield (b) over USHY samples (VVH = 20,000 h⁻¹, RH = 50%, 900 ppm of 1-MN) at 300 (■), 400 (▲) and 450 °C (*).

be due to the low concentration of aromatic compounds (900 ppm) in the feed.

In order to characterize the adsorbed products (coke), FT-IR spectra of the sample used for the reaction at 450 °C (4.1 wt% C) was taken after 7 h reaction (Fig. 3). The spectra shows the presence of bands characteristic of C=O in the 1700–1800 cm⁻¹ range and C=C in the 1400–1650 cm⁻¹ range [36]. Adsorbed products in the pores of the zeolite are thus mainly constituted of oxygenated aromatics compounds (C_xH_yO_z) as shown in the literature during xylene oxidation over Pd/zeolite (Scheme 1) [37].

1-MN is transformed into C_xH_yO_z compounds before its complete oxidation into carbon dioxide. The rates of transformation (ν_1 and ν_2) depend on the temperature. At low temperature (300 °C), the reaction rate ν_2 is very low and only C_xH_yO_z compounds are formed and retained initially in the pores of the

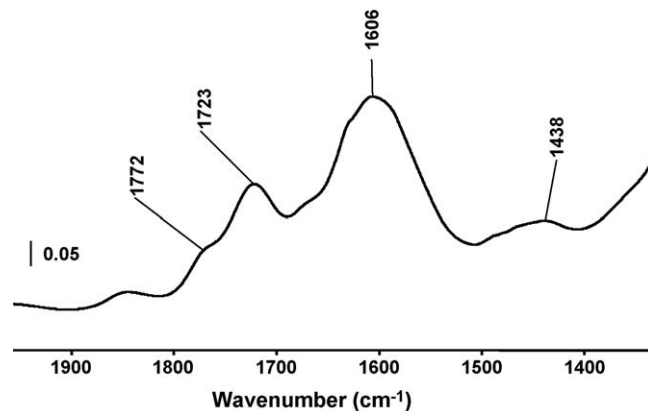
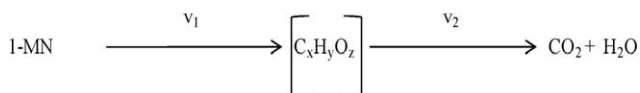


Fig. 3. Infrared spectra of USHY zeolite sample used, after 7 h reaction at 450 °C.

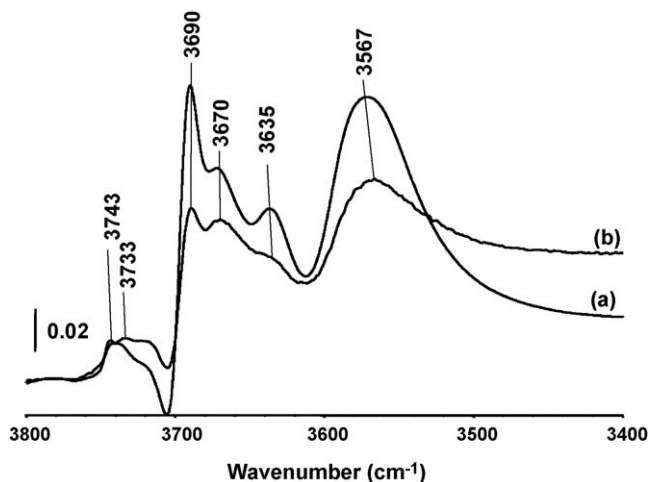
Table 2

USHY catalysts acidity characterization before and after reaction at 450 °C during 7 h.

USHY Catalysts	Acidity ($\mu\text{mol g}^{-1}$)	
	Brønsted	Lewis
Fresh	537	168
After reaction	138	115

**Scheme 1.** Represents the transformation of 1-MN over zeolite.

zeolite. When the temperature increases, the reaction rate v_2 increases since USHY zeolite possesses active acid sites able to transform $\text{C}_x\text{H}_y\text{O}_z$ into CO_2 . These sites, which are able to oxidize aromatics compounds into carbon dioxide are attributed to strong acid sites [33]. The sample used after 7 h for the reaction at 450 °C was characterized by pyridine adsorption followed by IR-spectroscopy. The acidity of the fresh sample and used sample were reported in Table 2. Over the used sample, decreases of 75% of Brønsted and 30% of Lewis sites were observed. This loss in acidity is attributed to coke adsorption over these sites. However, despite the large decrease of the number of acid sites and especially Brønsted ones measured on zeolites after reaction (Table 2), the catalyst continues to oxidize completely 1-MN into carbon dioxide at 450 °C (Fig. 2), whereas HFAU (47), which possesses 99 $\mu\text{mol g}^{-1}$ of Brønsted acid sites was only able to destroy 40% of 1-MN into carbon dioxide (Fig. 1). Scheme 1 could give an explanation of this where $\text{C}_x\text{H}_y\text{O}_z$ compounds are the intermediates of the reaction and are simultaneously formed and retained before the oxidation into carbon dioxide on the strong Brønsted acid sites of the zeolite. Fig. 4 shows IR spectra of the OH acids groups of the fresh sample and the sample after reaction at 450 °C. Six distinct OH bands are present in the IR spectra of the fresh zeolite at 3567, 3635, 3670, 3690, 3733 and 3743 cm^{-1} . Their assignments were proposed by several authors [38,39]. Thus, the 3567 and 3635 cm^{-1} bands are assigned to the hydroxyls located in sodalite cages and supercages, respectively. The 3690 cm^{-1} is assigned to Al–OH groups in extra-framework Al species, and the 3733 and 3743 cm^{-1} bands correspond to Si–OH silanols groups. The assignment of the 3670 cm^{-1} bands is not clear [39,40]. The

**Fig. 4.** Infrared spectra of OH groups over fresh USHY (a) and over the sample obtained after reaction at 450 °C (b).**Table 3**

Physicochemical properties of PtUSHY catalysts.

(%)	Pt dispersion ^a (%)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	Acidity ($\mu\text{mol g}^{-1}$)	
			Brønsted	Lewis
0		0.290	537	168
0.2	10	0.246	n.d.	n.d.
0.6	11	0.194	n.d.	n.d.
0.8	15	0.257	460	138
1.8	50	0.276	n.d.	n.d.

n.d.: not-determined.

^a Platinum dispersion is measured by carbon monoxide adsorption followed by IR spectroscopy.

coke deposition results in a reduction of the OH bands (Fig. 4). The OH bands concerned by this reduction are mainly the OH groups in the sodalite cages (3567 cm^{-1}), in the supercages (3635 cm^{-1}) and the Al–OH groups in extra-framework position (3690 cm^{-1}). The correlation between the decrease in Lewis acid sites (Table 2) and the reduction of the band at 3690 cm^{-1} , indicates that coke molecules are located in the zeolite porosity and near the extra-framework Al–OH groups.

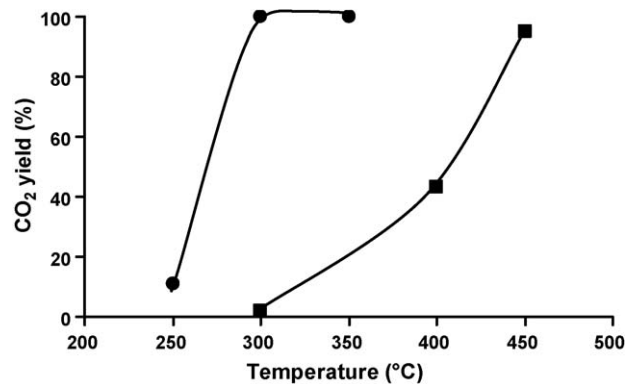
3.2. Platinum effect during 1-MN oxidation

3.2.1. Effect of 0.8% of platinum over USHY zeolite

Platinum showed a great catalytic activity to destroy naphthalene molecules [2,5,9,12,41]. Platinum effect was studied over USHY zeolite with 0.8% platinum content and in the 250–350 °C temperature range. Characterization of the catalyst is reported in Table 3. We can notice decreases in microporous volume and in acidity due to the presence of platinum. Fig. 5 shows the yield into carbon dioxide as function of reaction temperature for USHY and 0.8%PtUSHY. The presence of platinum improves the catalytic activity. A yield into carbon dioxide of 100% is obtained at 300 °C over 0.8%PtUSHY against 450 °C over the support without platinum.

3.2.2. Influence of platinum content

The influence of platinum content was studied for 1-MN oxidation at various temperatures. A series of PtUSHY catalysts with platinum content varying from 0 to 1.8 wt.% and platinum dispersion from 10 to 50% was used (Table 3). We noticed a decrease of the microporous volume due to the size of platinum particles present on the support (from 2.0 to 8.0 nm). The carbon dioxide yield reported after 6 h reaction, increased with reaction temperature and platinum content (Fig. 6). Whatever the platinum content (from 0.2 to 1.8 wt.%), PtUSHY catalysts were able to

**Fig. 5.** Carbon dioxide yield obtained after 6 h reaction as a function of the reaction temperature over USHY (■) and 0.8%PtUSHY catalysts (●) (VVH = 20,000 h⁻¹, RH = 50%, 1-MN = 900 ppm).

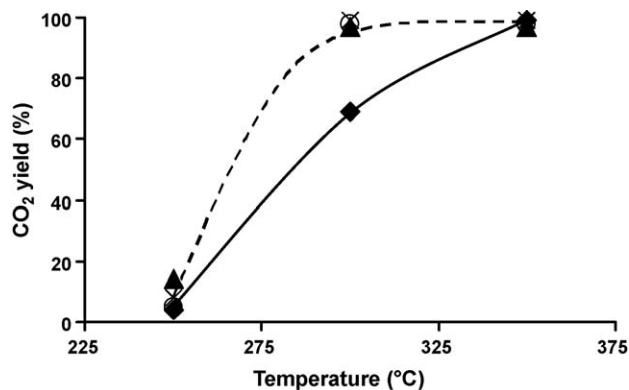


Fig. 6. Carbon dioxide yield obtained after 6 h reaction as a function of the reaction temperature over PtUSHY catalysts: 0.2% (◆), 0.6% (○), 0.8% (▲) and 1.8% (×) (VVH = 20,000 h⁻¹, RH = 50%, 1-MN = 900 ppm).

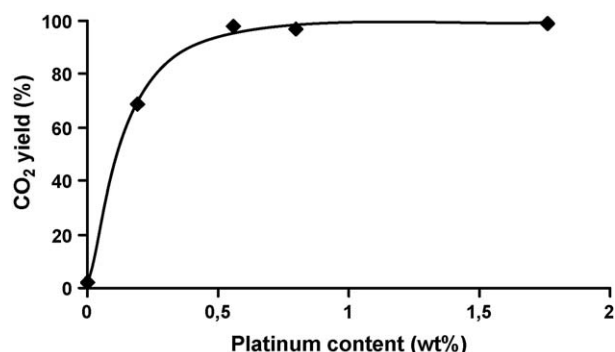
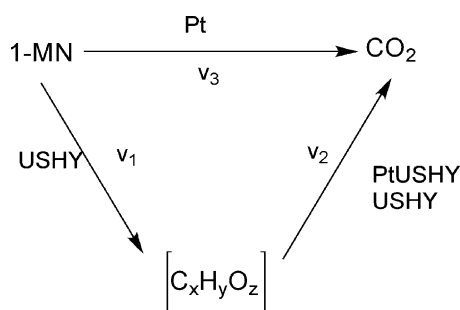


Fig. 7. Carbon dioxide yield after 7 h reaction as a function of platinum content over PtUSHY catalyst at 300 °C.

oxidize completely 1-MN at 350 °C against 450 °C over USHY. At 300 °C, carbon dioxide yield increased with platinum content and for Pt ≥ 0.5 wt% a total conversion is observed (Fig. 7). 1-MN oxidation into carbon dioxide depends on the platinum content: for platinum content between 0 and 0.5 wt%, the carbon dioxide yield increases. According to the Scheme 1, 1-MN is pre-transformed over zeolitic support into C_xH_yO_z compounds from 300 °C. With platinum addition, the reaction could be described by Scheme 2.

At low temperature (250 °C) whatever platinum content, the activity of the metal is low and Pt is not able to transform directly 1-MN into carbon dioxide (v₃). Until 300 °C over USHY zeolite, only C_xH_yO_z are formed (v₁). However, as exposed before, part of the platinum is located in the zeolite porosity. The proximity of platinum particles and C_xH_yO_z compounds both retained in the zeolite pores could lead the latter to be oxidized into carbon dioxide for platinum amounts higher than 0.2 wt% (v₂ increases as well as v₃). At higher temperatures (350 °C), platinum and zeolite



Scheme 2.

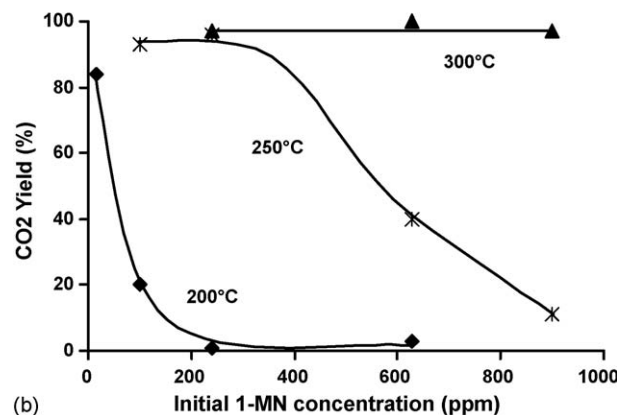
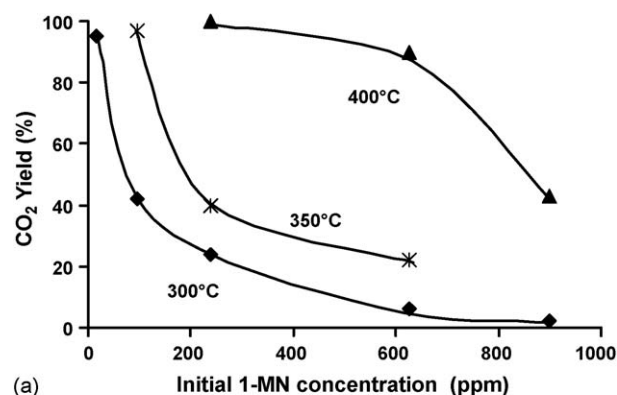


Fig. 8. Influence at different temperatures of initial 1-methylnaphthalene concentration (17–900 ppm) on carbon dioxide yield over USHY catalyst (a) and 0.8%PtUSHY catalyst (b), (VVH = 20,000 h⁻¹, RH = 50%).

are both able to oxidize C_xH_yO_z intermediates but the v₃ rate certainly strongly increases and Pt particles become the main active sites.

3.3. Effect of 1-MN concentration

The effect of 1-MN concentration (from 17 to 900 ppm) was established over USHY and 0.8%PtUSHY in the 200–400 °C temperature range (Fig. 8). Whatever the catalyst, the catalytic oxidation of 1-MN increases when the concentration in pollutant decreases. Thus, USHY zeolite is able to destroy completely into carbon dioxide 17 ppm of 1-MN from 300 °C (Fig. 8a). Likewise, 0.8%PtUSHY allows to oxidize low concentration of 1-MN (<17 ppm) from 200 °C (Fig. 8b). Over USHY, the reaction order in oxidation with respect to 1-MN is 0.9 at 300 °C, and the activation energy (E_a) calculated for 100 ppm between 300 and 350 °C is close to 61.1 kJ mol⁻¹. Moreover, the reaction order in oxidation with respect to 1-MN is estimated to 1 over 0.8%PtUSHY at 200 °C, and the activation energy (E_a) calculated for 100 ppm between 200 and 250 °C can be estimated to 41.7 kJ mol⁻¹.

The relative higher activity energies show that oxidation of 1-MN is not affected by external diffusion limitation since in such case it is generally assumed that activation energy is below 20 kJ mol⁻¹.

3.4. Effect of relative humidity

Relative humidity (RH) plays an important role on catalytic oxidation of PAHs. Water produced during the reaction and/or present in the feed affects catalytic behaviour of catalysts. In oxidation reaction, it was shown that water had negative effect on combustion reaction [42–44]. It has however been described a

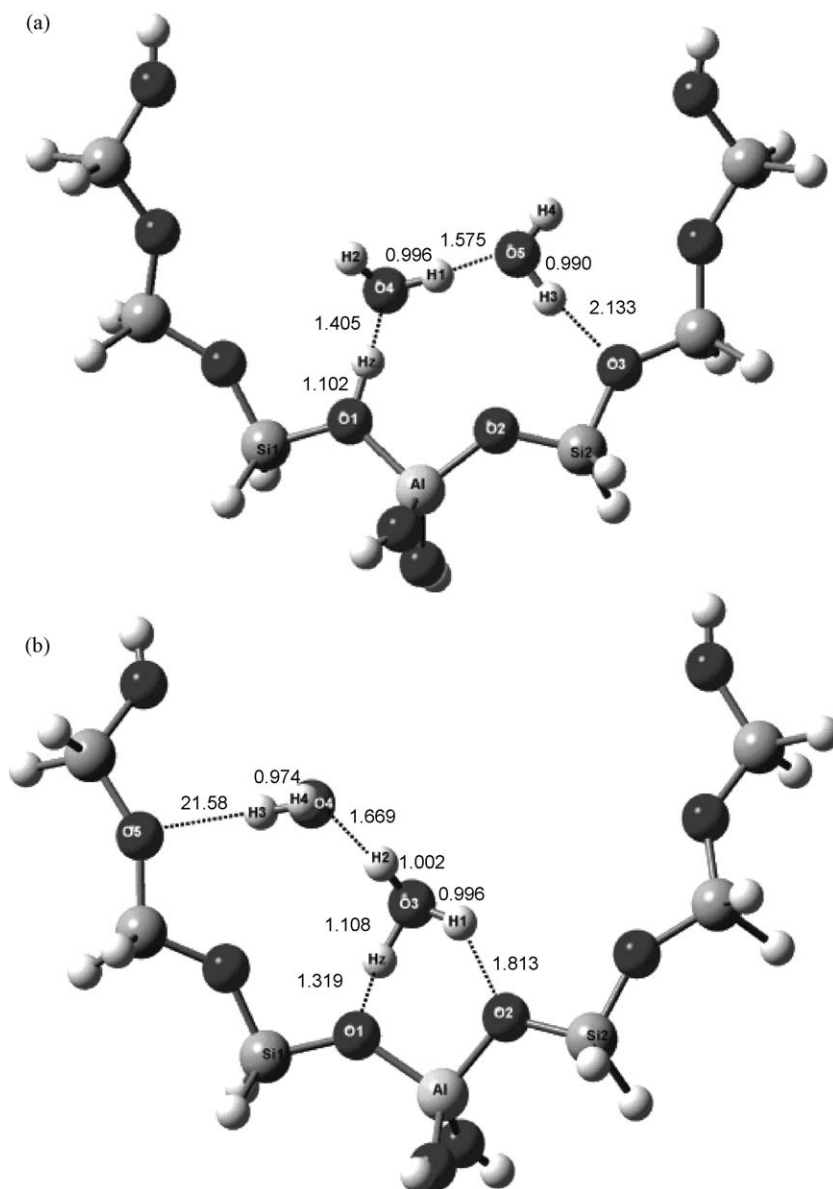


Fig. 9. Structure of the water dimer adsorbed over H-faujasite: the neutral complex form (a) and the ion-pair complex form (b). Reprinted with permission from [56]. Copyright 2005 American Chemical Society.

beneficial effect of steam during oxidation of chlorinated compounds over zeolite [45] and over Pt/zeolite [10]. During propane and propene oxidation, Marecot et al. [46] showed that water (up to 10%) had a beneficial effect over palladium catalyst prepared from chlorinated palladium precursor.

Theoretical works concerning water adsorption over protonic zeolite [47–49] suggest a proton transfer to an H_2O dimer, which leads to formation of protonated structure (ion-pair complex) [47,49,50]. These results highlight the existence of two different equilibrium adsorption structures for the interaction of an H_2O dimer with an acid site: the neutral dimer (Fig. 9a) is hydrogen bonded to the zeolite acid site (neutral complex), while the other protonated form is bounded to the anionic zeolite framework (ion-pair complex) to form an H_5O_2^+ ion (Fig. 9b).

Recently, Sazama et al. [51] showed that neutral complex of water were formed in the ZSM-5 and ferrierite zeolite at low vapour pressure. The increase of water concentration in the gas stream, favoured the formation of the ion-pair complex form (protonated species). Moreover, these authors show that pore structure of the zeolite affect the interaction of H_2O with zeolites.

Narrow zeolite channels and higher density of aluminium atoms in the zeolite framework preferentially stabilize small ionic cluster and the protonated cluster can be easily formed. But in the case of large pore zeolites (e.g. USHY), the same phenomenon would take place: at low water concentration, the neutral complex formation is favoured and for high water concentration ion-pair complex (H_5O_2^+) would be preferentially formed.

The effect of relative humidity (from 0 to 50%) was studied over USHY catalyst at 300 and 350 °C and over 0.8%PtUSHY at 200 and 250 °C for a 1-MN concentration of 100 ppm (Fig. 10). Whatever the catalyst and reaction temperature, two phenomena can be described. In absence of water, the catalysts activities are very high and 1-MN oxidation is total over USHY from 300 °C (Fig. 10a) and above 80% over 0.8%PtUSHY from 200 °C (Fig. 10b). The addition of water causes firstly a decrease in activity (up to 12% of relative humidity) then an increase for $\text{RH} > 12\%$. This increase in activity was better observed at high temperature (350 °C over USHY and 250 °C over 0.8%PtUSHY). At lower temperature, a quasi-plateau is observed (about 20% of carbon dioxide yield at 200 °C for 0.8%PtUSHY and 40% at 300 °C for USHY). Initially, the beneficial

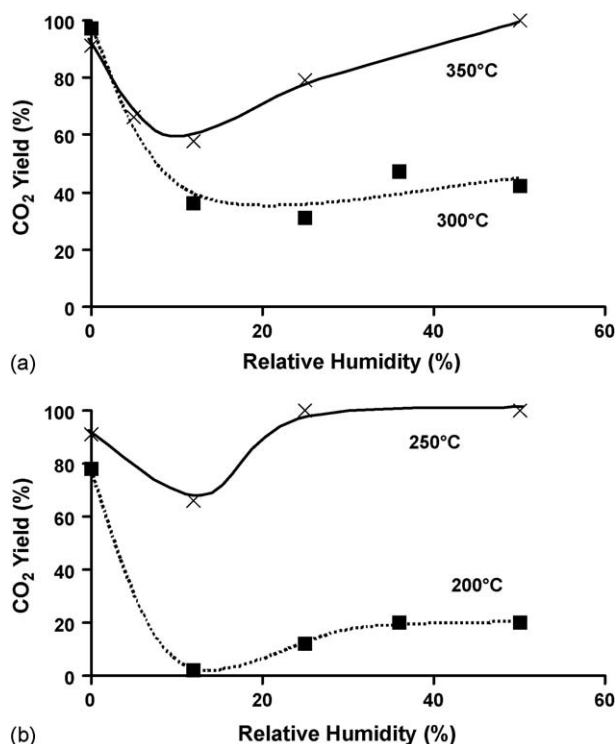


Fig. 10. Influence of relative humidity on carbon dioxide yield at different temperatures over USHY catalyst (a) and over 0.8%PtUSHY (b), (100 ppm of 1-MN, VVH = 20,000 h⁻¹).

effect of water at higher content could be related to the removal of coke deposited over the catalyst. Nevertheless, elemental analysis carried on 0.8%PtUSHY used samples showed that the carbon contents were of 1.2, 12.2, 14.1 and 12.7 wt% for respectively 0, 12, 25 and 36% of relative humidity. The main effect of water is therefore probably not associated with coke removal.

In order to explain these results, several assumptions could then be formulated.

- (i) relative humidity $\leq 12\%$:
over USHY catalyst

Water inhibitory effect over the strong hydrophilic character of aluminium-rich zeolites is observed through the formation of an H₂O dimer:neutral complex form.

According to our results, water present in low concentration plays an inhibitory effect over the catalytic activity of the USHY zeolites. The decrease of the carbon dioxide yield observed can be related to the strong hydrophilic character of USHY [45,52]. H-zeolite adsorbs water at low pressures and water dimer neutral complex could be formed over the strong acid sites, which are active in oxidation reaction leading to an inhibitory effect. Furthermore, the dimer neutral complex of water can create a diffusional limitation of 1-MN molecule resulting to a lower carbon dioxide yield over USHY.

over PtUSHY catalyst

At 200 °C in absence of water (Fig. 10b), carbon dioxide yield is of 80% and metallic sites are active for 1-MN oxidation into carbon dioxide. According to Fig. 10b for HR < 12%, it is also possible that water reacts with PtO to form Pt(OH)₂ at the PtO surface, effectively blocking the access of 1-MN to the active PtO phase. A similar inhibitory effect of water was observed by Ribeiro et al. [42] over palladium catalyst during the oxidation

of methane. The Pt(OH)₂ formation was explained in some studies by water dissociation on platinum and palladium [53–55], leading to H and OH species. However, the recombination is very fast when only water is present.

- (ii) In the case of a relative humidity higher than 12%:

Whatever the catalyst, when the relative humidity increases, the carbon dioxide yield increases (Fig. 10).
over USHY catalyst

For RH > 12%, ion-pair complex (H₅O₂⁺) could be formed. This complex formation could generate a low acidity leading to the increase of carbon dioxide yield via the formation of more oxygenated compounds C_xH_yO_z (z > 2), which formed at low relative humidity.

Another explanation of the observed behaviour could be the thermodynamic instability of the adsorbed dimer ion-pair complex consequently to the increase of temperature (e.g. 350 °C). The amount of acid sites affected by the formation of this ion-pair complex decreases and thus, sites that can act again for the oxidation reaction of 1-MN are released.

over PtUSHY catalyst

The water dimer ion-pair complex could be preferentially adsorbed over zeolites sites leading to the liberation of a part of PtO phase. However, at RH > 12%, the water complex formed over PtO could also be instable when the temperature increases (e.g. 250 °C) leading to a liberation of a large part of PtO active phase for 1-MN oxidation.

4. Conclusions

Zeolites are able to transform PAHs such as 1-methylnaphthalene into carbon dioxide. However, the number of acid sites is an important parameter for this reaction. Thus, USHY zeolites, which possess a low Si/Al ratio and a high number of Brønsted acid sites are appropriate supports.

Catalytic oxidation of 1-MN (900 ppm) was carried out over USHY zeolite. During this study, no aromatic by-products were observed. Over USHY, complete oxidation of 1-MN into carbon dioxide was achieved at 450 °C. It was shown that USHY transforms and retains in its pores 1-MN into oxygenated compounds before complete oxidation. The presence of platinum improves the catalytic activity and total oxidation of the pollutant was obtained at 300 °C with 0.8 wt% platinum content on the USHY. However, USHY catalysts are able to destroy about 20 ppm of 1-MN at 300 °C without platinum addition and with a total selectivity in CO₂, which make them good candidates for the treatment of effluents slightly charged in PAHs.

The study of water content has shown the important role of this molecule during oxidation reaction. For low water content, an inhibitory effect was found on the carbon dioxide yield. The explanations are the adsorption of water molecule over the strong hydrophilic sites of USHY zeolite and the water cluster formation from H₂O dimer (neutral complex form). Over 0.8%PtUSHY, water molecules can be adsorbed over the PtO phase and involves Pt(OH)₂ formation that blocks access of 1-MN to the active PtO phase. For high water content, the presence of water had a promoter effect over the carbon dioxide yield. Two explanations are proposed: the first one is the increase in carbon dioxide yield due to the thermodynamic instability of H₂O dimer over the acid and metallic sites. The second one is the formation of an ion-pair complex form. This complex (H₅O₂⁺) could also participate to the oxidation reaction leading to the formation of more oxygenated

compounds. These compounds would be more easily degraded in carbon dioxide over USHY and PtUSHY catalysts.

Acknowledgements

S.C. Marie-Rose gratefully acknowledges the Agence de l'Environnement et de la Maîtrise de l'Energie (ADEME) and the Région Poitou-Charentes for his Ph.D. grant.

References

- [1] K. Breivik, R. Alcock, Y.-F. Li, R.E. Bailey, H. Fiedler, J.M. Pacyna, *Environmental Pollution* 128 (2004) 3–16.
- [2] X.-W. Zhang, S.-C. Shen, L.E. Yu, S. Kawi, K. Hidajat, K.Y. SimonNg, *Applied Catalysis A: General* 250 (2003) 341–352.
- [3] G. Saracco, V. Specchia, *Chemical Engineering Science* 55 (2000) 897–908.
- [4] J.J. Spiney, *Industrial & Engineering Chemistry Research* 26 (1987) 2165.
- [5] X.-W. Zhang, S.-C. Shen, K. Hidajat, S. Kawi, L.E. Yu, K.Y. SimonNg, *Catalysis Letters* 96 (2004) 87–96.
- [6] J. Tsou, L. Pinard, P. Magnoux, J.L. Figueiredo, M. Guisnet, *Applied Catalysis B: Environmental* 46 (2003) 371–379.
- [7] S. Ordóñez, L. Bello, H. Sastre, R. Rosal, F.V. Díez, *Applied Catalysis B: Environmental* 38 (2002) 139–149.
- [8] P. Papaefthimiou, T. Ioannides, X.E. Verykios, *Applied Catalysis B: Environmental* 13 (1997) 175–184.
- [9] J.-L. Shie, C.-Y. Chang, J.-H. Chen, W.-T. Tsai, Y.-H. Chen, C.-S. Chiou, C.-F. Chang, *Applied Catalysis B: Environmental* 58 (2005) 289–297.
- [10] M. Taralunga, J. Mijoin, P. Magnoux, *Applied Catalysis B: Environmental* 60 (2005) 163–171.
- [11] R.W. van den Brink, R. Louw, P. Mulder, *Applied Catalysis B: Environmental* 25 (2000) 229–237.
- [12] J. Carno, M. Berg, S. Jaras, *Fuel* 75 (1996) 959–965.
- [13] M. Ferrandon, J. Carno, S. Jaras, E. Bjornbom, *Applied Catalysis A: General* 180 (1999) 153–161.
- [14] M. Ferrandon, J. Carno, S. Jaras, E. Bjornbom, *Applied Catalysis A: General* 180 (1999) 141–151.
- [15] P. Liljelind, J. Unsworth, O. Maaskant, S. Marklund, *Chemosphere* 42 (2001) 615–623.
- [16] R. Weber, T. Sakurai, H. Hagenmaier, *Applied Catalysis B: Environmental* 20 (1999) 249–256.
- [17] S. Albonetti, S. Blasioli, R. Bonelli, J.E. Mengou, S. Scirè, F. Trifirò, *Applied Catalysis A: General* 341 (2008) 18–25.
- [18] J.F. Lamonier, A.B. Boutoundou, C. Gennequin, M.J. Perez-Zurita, S. Siffert, A. Aboukais, *Catalysis Letters* 118 (2007) 165–172.
- [19] R. Lopez-Fonseca, J.I. Gutierrez-Ortiz, J.R. Gonzalez-Velasco, *Applied Catalysis A: General* 271 (2004) 39–46.
- [20] M. Taralunga, B. Innocent, J. Mijoin, P. Magnoux, *Applied Catalysis B: Environmental* 75 (2007) 139–146.
- [21] M. Taralunga, J. Mijoin, P. Magnoux, *Catalysis Communications* 7 (2006) 115–121.
- [22] F. Klingstedt, A. Kalantar Neyestanaki, L.E. Lindfors, T. Salmi, T. Heikkilä, E. Laine, *Applied Catalysis A: General* 239 (2003) 229–240.
- [23] H.L. Tidahy, S. Siffert, J.F. Lamonier, R. Cousin, E.A. Zhilinskaya, A. Aboukais, B.L. Su, X. Canet, G. De Weireld, M. Frère, J.M. Giraudon, G. Leclercq, *Applied Catalysis B: Environmental* 70 (2007) 377–383.
- [24] S.C. Marie Rose, J. Mijoin, P. Magnoux, M. Taralunga, X. Chaucherie, E. Fiani, *Organohalogen Compounds* 70 (2008) 2216–2219.
- [25] C.C. Yang, S.H. Chang, B.Z. Hong, K.H. Chi, M.B. Chang, *Chemosphere* 73 (2008) 890–895.
- [26] S. Krishnamoorthy, J.A. Rivas, M.D. Amiridis, *Journal of Catalysis* 193 (2000) 264–272.
- [27] S. Lomnicki, J. Lichtenberger, Z. Xu, M. Waters, J. Kosman, M.D. Amiridis, *Applied Catalysis B: Environmental* 46 (2003) 105–119.
- [28] S. Scirè, S. Minicò, C. Crisafulli, G. Burgio, V. Giuffrida, G.G.R. Aiello, F. Testa, *Studies in Surface Science and Catalysis*, Elsevier, 2002, pp. 1023–1030.
- [29] S. Khabtou, T. Chevreau, J.C. Lavalley, *Microporous Materials* 3 (1994) 133–148.
- [30] C. Binet, A. Jodi, J.C. Lavalley, *Journal of the Chemical Society, Faraday Transactions* 88 (1992) 2079.
- [31] J. Lynch, F. Raatz, P. Dufresne, *Zeolites* 7 (1987) 333–340.
- [32] Q.L. Wang, G. Giannetto, M. Torrealba, G. Perot, C. Kappenstein, M. Guisnet, *Journal of Catalysis* 130 (1991) 459–470.
- [33] K. Moljord, P. Magnoux, M. Guisnet, *Catalysis Letters* 28 (1994) 53–59.
- [34] K. Moljord, P. Magnoux, M. Guisnet, *Applied Catalysis A: General* 121 (1995) 245–259.
- [35] K. Moljord, P. Magnoux, M. Guisnet, *Applied Catalysis A: General* 122 (1995) 21–32.
- [36] J. Ryczkowski, *Catalysis Today* 68 (2001) 263–381.
- [37] M. Guisnet, P. Dégé, P. Magnoux, *Applied Catalysis B: Environmental* 20 (1999) 1–13.
- [38] H.S. Cerqueira, P. Ayrault, J. Datka, M. Guisnet, *Microporous and Mesoporous Materials* 38 (2000) 197–205.
- [39] P.O. Fritz, J.H. Lunsford, *Journal of Catalysis* 118 (1989) 85–98.
- [40] W. Lutz, E. Löfler, M. Fechtelkord, E. Schreier, R. Bertram, S.-K.I.A.Y.S.U. Hakze-Chon, *Studies in Surface Science and Catalysis*, Elsevier, 1997, pp. 439–446.
- [41] T. Garcia, B. Solsona, S.H. Taylor, *Applied Catalysis B: Environmental* 66 (2006) 92–99.
- [42] F.H. Ribeiro, M. Chow, R.A. Dallabetta, *Journal of Catalysis* 146 (1994) 537–544.
- [43] C.F. Cullis, B.M. Willatt, *Journal of Catalysis* 86 (1984) 187–200.
- [44] C.F. Cullis, T.G. Nevell, D.L. Trimm, *Journal of the Chemical Society, Faraday Transactions* 1 (68) (1972) 1406–1412.
- [45] R. Lopez-Fonseca, A. Aranzabal, J.I. Gutierrez-Ortiz, J.I. Alvarez-Urriarte, J.R. Gonzalez-Velasco, *Applied Catalysis B: Environmental* 30 (2001) 303–313.
- [46] P. Marécot, A. Fakche, B. Kellali, G. Mabilon, P. Prigent, J. Barbier, *Applied Catalysis B: Environmental* 3 (1994) 283–294.
- [47] M. Krossner, J. Sauer, *Journal of Physical Chemistry* 100 (1996) 6199–6211.
- [48] S.A. Zygmunt, L.A. Curtiss, L.E. Iton, *Journal of Physical Chemistry B* 105 (2001) 3034–3038.
- [49] S.A. Zygmunt, L.A. Curtiss, L.E. Iton, M.K. Erhardt, *Journal of Physical Chemistry* 100 (1996) 6663–6671.
- [50] D.H. Olson, S.A. Zygmunt, M.K. Erhardt, L.A. Curtiss, L.E. Iton, *Zeolites* 18 (1997) 347–349.
- [51] P. Sazama, Z. Tvarůžková, H. Jirglová, Z. Sobalík, *Studies in Surface Science and Catalysis* 174 (2008) 821–824.
- [52] J.A. Rabo, G.J. Gajda, *Catalysis Reviews* 31 (1989) 385–430.
- [53] W.G. McNaught, C. Kemball, H.F. Leach, *Journal of Catalysis* 34 (1974) 98–105.
- [54] K. Otsuka, M. Hatano, A. Morikawa, *Journal of Catalysis* 79 (1983) 493–496.
- [55] J.M. Heras, L. Viscido, *Catalysis Reviews* 30 (1988) 281–338.
- [56] S. Jungsuttiwong, J. Limtrakul, T.N. Truong, *Journal of Physical Chemistry B* 109 (2005) 13342–13351.